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THE INFLUENCE OF CERTAIN FUNCTIONAL GROUPS IN A FUEL MOLECULE ON THE BURNING RATE OF CONDENSED SYSTEMS

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THE INFLUENCE OF CERTAIN FUNCTIONAL GROUPS IN A FUEL MOLECULE ON THE BURNING RATE OF CONDENSED SYSTEMS

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The influence of the chemical structure of an organic fuel on the burning rate of solid fuel/solid oxidizer mixtures has, up to the present time, been examined in only a few works. We can mention [1], where the authors conclude that the burning rate of condensed systems depends on the calorific value of the fuel or, if the calorific values are equal, on its chemical structure.

In this paper we study the burning of mixtures of ammonium perchlorate (APC) with fuels of the diphenyl series and the azobenzene series. Within the limits of each series the fuel is distinguished by the number of amino groups. We also studied the following organic acids: succinic and aminosuccinic, and benzoic and aminobenzoic.

In all tests we used vibrated APC with a particle size of 7 μ. The fuels were first ground in a mortar and sifted through a 90-μ sieve, after which they were placed in a desiccator and held over P_2O_5 for 24 hours. The powdered components were blended on tracing paper for 40 minutes using a rubber stopper. The obtained mixture was pressed into small brass beakers having inside diameter of 10 mm.

The compression pressure was 4000 kg/cm^2. The specimens were burned in a constant-pressure bomb in nitrogen at $P \leq 100$ atm. The average burning rate was measured using a piezoelectric pressure transducer with a loop oscillograph. As a control, several specimens were burned in organic glass tubes; here we detected no differences in the burning rates of the compositions in the various casings.

The names of the fuels and the maximum burning rates of mixtures of these fuels with APC at $P = 100$ atm are given in the table; the last column contains data on the ignition delay time of these compositions under isothermal conditions at 400°C. Figures 1-3 give the burning rate[1] vs pressure for these compositions at $\alpha = \alpha_{u\ max}$.

From Figs. 1-3 and the table it follows that the introduction of the $-NH_2$ group into a fuel molecule in all cases increases the burning rate; this increase is the greater, the higher the percentage of $-NH_2$ groups in the molecule. In the diphenyl series we found that the burning rate of a mixture of APC and *p*-phenylenediamine is higher than with benzidine, and with benzidine it is higher than with aminodiphenyl (Fig. 1). For the azobenzene series, analogously, a mixture with chrysoidine burns faster than one with aminoazobenzene. However, the influence of the $-NH_2$ groups on the burning rate of compositions in the azobenzene series is lower than in the diphenyl series.

The additional introduction of the methyl group into a fuel molecule insignificantly increases the burning rate (compare the data for *o*-tolidine and benzidine and for aminoazotoluene and aminoazobenzene in the table). It should be noted that introduction of the methyl group has a lesser accelerating influence than the introduction of the amino group. The burning rate of mixtures with

[1] For the diphenyl series the stoichiometric coefficient with maximum burning rate $\alpha_{u\ max} = 0.8$; for the azobenzene series $\alpha_{u\ max} = 0.5$; for succinic and aminosuccinic acids $\alpha_{u\ max} = 1.2$; for benzoic and aminobenzoic acids $\alpha_{u\ max} = 0.7$.

Maximum burning rate of various fuels with APC (p = 100 atm)

Fuel	u, mm/s	τ_3, s
Diphenyl	10.5	62
Aminodiphenyl	17.7	10
Benzidine	21.5	8.5
o-Tolidine	26.0	10
p-Phenylenediamine[1]	28.0	1.0
Azobenzene	15.4	40
Aminoazobenzene	16.0	16
Chrysoidine	22.7	—
o-Aminoazotoluene	19.1	9.5
Succinic acid	5.2	85
Aminosuccinic acid	10.6	14.0
Benzoic acid	13.8	65
Aminobenzoic acid	18.7	9.0

[1] We have arbitrarily included p-phenylenediamine in the diphenyl series.

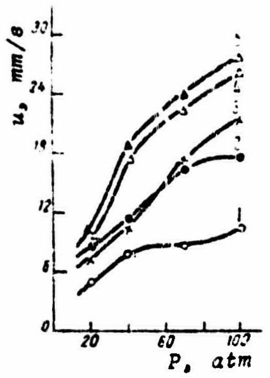

Fig. 1. Burning rate vs pressure for mixtures of APC with the following fuels: 1 – diphenyl; 2 – aminodiphenyl; 3 – benzidine; 4 – o-tolidene; 5 – p-phenylenediamine.

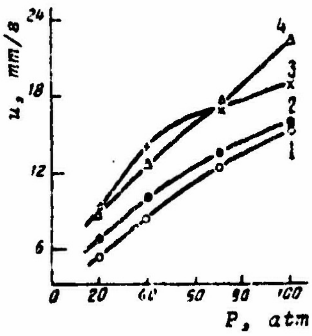

Fig. 2. Burning rate vs pressure for mixtures of APC with the following fuels: 1 – azobenzene; 2 – aminoazobenzene; 3 – o-aminoazotoluene; 4 – chrysoidine.

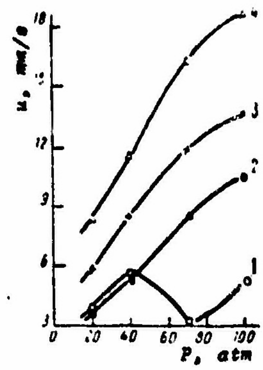

Fig. 3. Burning rate vs pressure for mixtures of APC with the following acids: 1 – succinic; 2 – aminosuccinic; 3 – benzoic; 4 – aminobenzoic.

chrysoidine is higher than for those with o-aminoazotoluene.

For compositions with succinic acid we observe an anomalous dependence of burning rate on pressure. The reasons for these anomalies have been examined in detail in [2]. The introduction of the amino group into succinic acid not only increases the burning rate but at the same time changes completely the form of the dependence of burning rate on pressure (Fig. 3).

From the table it also follows that the presence of $-NH_2$ or $-CH_3$ groups in a fuel molecule reduces the ignition delay time ($\tau_з$). Let us note that within each series we observe a correspondence between $\tau_з$ and the burning rate of the compositions: the lower the $\tau_з$, the higher the burning rate.

There can be various reasons for an increase in burning rate with the introduction of functional groups into a molecule. Certain fuels containing $-NH_2$ groups can interact with APC with formation of corresponding organic perchlorates; we know [3, 4] that the burning rate of a number of them is high. The burning rate of *p*-phenylenediamine diperchlorate at 40 atm is 58 mm/s, while that of benzidine perchlorate is 25.8 mm/s.

However, in our case the studies of mixtures of fuels with APC showed that at room temperature the fuel and APC do not interact. IR spectra of the heated layer of extinguished specimens also showed that with burning of the investigated compositions no organic perchlorates were observed in the surface layer of the specimens. Consequently, there must be another reason for the increased burning rate when $-NH_2$ and $-CH_3$ groups are introduced into a fuel molecule.

In our opinion, the basic reason for this is the change in composition of the fuel pyrolysis products. This question, however, requires further study.

CONCLUSIONS

1. We have studied the burning of finely-dispersed mixtures of ammonium perchlorate with fuels of the diphenyl and azobenzene series (and also with four organic acids) containing $-NH_2$ and $-CH_3$ groups in the molecule.

2. The introduction of $-NH_2$ and $-CH_3$ groups into a fuel molecule increases the burning rate, the more intensely the higher the percentage of these groups in the fuel molecule.

3. Within each series of fuels there is a correspondence between the ignition delay of the compositions and their burning rate: the shorter the delay time, the higher the burning rate.

4. Higher burning rates of mixtures of APC with fuels containing $-NH_2$ and $-CH_3$ groups are possibly associated with the higher reaction capability of the gasification products of these fuels.

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